

**Title: NOXIDIZER™ SYSTEM FOR HIGH-LEVEL NO_x REDUCTION
PRELIMINARY TEST RESULTS AT MSE TECHNOLOGY
APPLICATIONS, INC.'S OFFGAS TEST UNIT**

Authors: Daniel M. Battleson, Steve E. Johnson, John L. Montgomery, Sergei Babko, Clarence Whitworth

danmb@in-tch.com
(406) 494-7287
(406) 494-7230
MSE Technology Applications, Inc.
P.O. Box 4078
200 Technology Way
Butte, Montana 59701

PROBLEM

For more than three decades, the Idaho National Engineering and Environmental Laboratory (INEEL) has used a calciner plant to treat radioactive and hazardous liquids, converting millions of gallons of potentially troublesome liquids into a more stable form. The New Waste Calcination Facility (NWCF) at the INEEL, which was built in 1982 prior to the enactment of many of today's hazardous waste and air-quality laws, now faces an uncertain future given the proposed U.S. Environmental Protection Agency's (EPA) new Maximum Achievable Control Technology (MACT) requirements.

As a result of thermal processing of high nitric acid-laden waste, offgas from the NWCF contains approximately 30,000 parts per million volume (ppmv) of oxides of nitrogen (NO_x) at a nitrogen dioxide (NO₂) to nitrogen oxide (NO) ratio of 8:1. This high level of NO_x makes it difficult, if not impossible, to obtain quality standard EPA isokinetic sampling as required to verify compliance with the new MACT rule because of excessive acid condensation in the sampling train. Also, an orange cloud is sometimes present in the NWCF area, which also increases public pressure to reduce NO_x emission levels. After evaluating alternative technologies, including selective catalytic reactors, a multistage combustion NO_x removal system was selected by the NWCF as the most feasible technology to control NO_x emissions.

Staged-combustion incinerators have been used in many industrial applications to reduce NO_x emissions from waste gas streams having relatively low NO_x concentrations. Data is needed on the use of staged combustion on waste gas streams having high-level NO_x concentrations and relatively low organic concentrations prior to installing a full-scale NO_x removal system at the NWCF.

MSE Technology Applications, Inc.'s (MSE) Controlled Emissions Demonstration (CED) Project, sponsored by the U.S. Department of Energy (DOE) Mixed Waste Focus Area (EM-50), focuses on installation, testing, and evaluation of state-of-the-art offgas treatment technologies and monitoring equipment. MSE was selected

to install and test a pilot-scale multistage combustion NO_x removal system. The objectives of this project are to set up process conditions similar to the NWCF's offgas and NO_x emission levels, test the performance of the NO_x removal system, report the test results, and make recommendations for a scaleup of the process for the NWCF.

SUPPORT SYSTEM DESCRIPTION

The NO_x treatment test-bed section is installed in the MSE slipstream test bed (SSTB). The primary thermal driver, a 1.6-million British thermal units per hour (Btu/hr) oxygen (O₂)-enriched natural gas-fired burner, is installed upstream of the SSTB. This burner can generate NO_x concentration levels of 3,500 ppmv, which are predominately NO₂. Downstream of the primary burner is a 540,000-Btu/hr natural gas-fired secondary combustion chamber. Approximately 2.4 pounds per minute mass flow of offgas will be drawn from the main offgas system to supply approximately 3,500 ppmv of initial NO_x-laden gas to the NO_x removal test system. Typically 8% carbon dioxide (CO₂) levels will be present in this offgas.

The main NO_x content in the offgas feed to the NOxidizer™ was generated by injecting 6 molar nitric acid into an electrically heated flameless oxidizer.

An in-line electric heater installed upstream of the flameless oxidizer preheats the temperature of the offgas to approximately 900 EF to 1,000 EF. The preheating enhances nitric acid vaporization and subsequent conversion to NO_x within the electric oxidizer.

Nitric acid is injected using a metering pump and atomizing nozzle injector into the offgas piping through ports located immediately upstream of a flameless oxidizer. The flameless oxidizer unit will control the offgas temperature to approximately 1,000 EF at the outlet. This temperature, combined with a gas residence time of 6 to 8 seconds in the heating unit, converts the nitric acid into the target NO₂/NO speciation ratio of 2:1. The stream composition analyzer is configured downstream of the electric flameless oxidizer unit to monitor offgas conditions. The NO_x-laden offgas is then piped to the experimental multistage NO_x removal unit.

NOXIDIZER® NO_x REMOVAL SYSTEM PROCESS DESCRIPTION

The staged-combustion approach involves initial combustion under O₂-deficient conditions, followed by offgas cooling and final combustion under excess O₂ conditions. The approach takes advantage of the basic thermodynamics of NO_x formation, which is favored by excess O₂ and temperatures above 2,400 EF.

The NO_x removal system tested is a three-stage process. The first stage (offgas supplemented with natural gas) will burn fuel with an expected flame temperature near 2,600 EF and a residence time of approximately 2 seconds. Both existing test data and theoretical models indicate that under these conditions NO_x and the other offgas constituents will react to form nitrogen (N₂), CO₂, water, carbon monoxide (CO), and hydrogen (H₂),

i.e., the NO_x will convert to N_2 . The offgas at this point has residual fuel value in the form of CO and H_2 and may also have fuel value in the form of partially burned hydrocarbons.

In the second stage, the offgas is water-quenched to approximately 1,500 EF to limit reformation of NO_x in the subsequent oxidizing stage and stay above the self-ignition temperature of CO .

In the third stage, O_2 is added to burn the residual CO , H_2 , and any unburned hydrocarbons. Sufficient O_2 is added to maintain the stack at 1.5 to 2% excess O_2 . The temperature at this stage will be maintained at 1,800 EF to 2,000 EF by addition of quench water at the prior stage. This temperature permits conversion of residual fuel value to CO_2 without reforming NO_x . The residence time in this stage will be approximately 1 second (chosen primarily to permit conversion of CO to CO_2).

NO_x -speciation and stream-composition continuous emissions monitoring system analyzers are installed upstream and downstream of the NO_x removal system to determine the NO_x reduction capability of the multistage combustion process.

PRELIMINARY TEST RESULTS

MSE tested the NO_x reduction capabilities of the reduction system in air containing up to 31,000 ppmv of NO_x at varying (up to 2:1) NO_2/NO ratios.

Testing at the time of this writing shows the NOxidizer™ system reducing NO_x by an average 99.2% with best readings at 99.6%. On a mass basis, removing the diluting masses of combustion air and natural gas results in 99.3% of the NO_x being removed. This meets the expectations of the test design. The actual operating point for maximum NO_x removal was still being optimized at the time of this writing. The NO_x removal seems to be mostly driven by the temperature difference between the quench section and the re-oxidizer sections.

Even though the NO_2 to NO ratio of the NWCF of 8:1 was not attained, it is believed to be a nonissue, because of the residence time and chemical processes involved.

Issues of process optimization are still being resolved as testing continues. The presentation that accompanies this summary report will have more complete test result information with further explanations.

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